



**CALIFORNIA REGIONAL PM<sub>10</sub>/PM<sub>2.5</sub> AIR QUALITY STUDY (CRPAQS)  
INITIAL DATA ANALYSIS OF CRPAQS FIELD PROGRAM MEASUREMENTS**

**Proposal**

submitted to  
San Joaquin Valleywide Air Pollution Study Agency/California Air Resource Board

by

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## 1. INTRODUCTION

Atmospheric and Environmental Research, Inc. (AER) is pleased to respond to the Request for Proposals (RfP) issued by the California Air Resources Board (ARB) on behalf of the San Joaquin Valleywide Air Pollution Study Agency on the Initial Data Analysis of Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS) Field Program Measurements. This proposal addresses Questions 2.7 and 6.1 through 6.3.

### 1.1 Background

The background for CRPAQS is summarized in the RfP. CRPAQS, together with its planning study IMS 95 and routine data collection activities, provides a comprehensive data base to understand the formation of PM in the San Joaquin Valley (SJV). Several questions are posed in the RfP. These questions are of interest to scientists and decision makers and have shaped the design of the CRPAQS field program.

AER has systematically assimilated data from the 1995 Integrated Monitoring Study (IMS 95) into a conceptual framework (Pun and Seigneur, 1999). Major data gaps were identified in that study, including:

- Abundance of ammonia relative to nitric acid as a function of location
- Pathways for the formation of nitrate as a function of location
- Sensitivity of nitrate to precursors as a function of location
- Formation of secondary organic aerosols (SOA)
- Relationships between sulfate, nitrate, and ozone (O<sub>3</sub>)
- Transport mechanisms for “regional distribution” of particulate matter (PM)
- The role of dry deposition
- The contribution of primary organic compounds (OC) and wind blown dust

CRPAQS provides an excellent opportunity to refine the conceptual understanding based on new data. In particular, it provides a comprehensive data base for the investigation of the related roles of chemical reactions and transport. For example, where do chemical reactions take place? Is PM or its precursors transported over long distances? We outline our approach and objectives in this proposal.

### 1.2 Objectives

The following questions posed in the RfP are addressed in this proposal.

Question 2.7.

- Where and when do elevated ozone concentrations correspond to excessive PM<sub>2.5</sub> concentrations?
- What fraction of the PM<sub>2.5</sub> corresponds to photochemical end-products?

Question 6.1.

- What is the distribution of PM (including chemical composition) and precursor species among phases (gas, liquid, and aerosol)?

- What chemical and physical mechanisms contribute to the observed phase distributions?
- How does this vary in space and time?
- How does the phase distribution (and chemical composition) vary before, during, and after fog events?

Question 6.2.

- Where and when do precursors (VOC, NO<sub>x</sub>, NH<sub>3</sub>, HNO<sub>3</sub>, SO<sub>2</sub>) limit the formation of secondary sulfates and nitrates?
- How is NO<sub>x</sub> oxidized to nitric acid under clear sky versus cloudy/foggy conditions?
- How much ozone and precursor species are above the valleywide layer and how much gets into the mixed layer?

Question 6.3.

- To what extent is the regional nature of secondary ammonium nitrate and ammonium sulfate due to well-defined transport between upwind and downwind regions due or caused by slow diffusion near the surface over multi-day stagnation periods?
- How do primary particles generated from residential combustion, vehicle exhaust, cooking, and road dust in an urban area arrive at non-urban areas and other distant urban areas under low wind, stagnant surface conditions?
- How do elevated oxides of nitrogen emissions from industrial sources get into the shallow mixed layer?

### 1.3 Overview of Technical Approach and Synergies

AER assimilated data from IMS 95 into a conceptual model (Pun and Seigneur, 1999) based on chemical composition and transport processes (advection, vertical mixing, wet and dry deposition). The framework for analyzing chemical composition is illustrated in Figure 1-1. CRPAQS provides the perfect opportunity to update and refine the conceptual model. Our main goals are as follows.

- (1) To determine if aspects of the conceptual framework are generally correct as a function of season, types of PM episodes, location, and time (1995 vs. 2000-2001)
- (2) To address key data gaps identified in that conceptual framework using data from CRPAQS

Our approach is to combine data analyses, some focused modeling, and the assimilation of the results of some other tasks described in the RfP.

Tasks 1, 2, and 4 will provide a detailed characterization of PM and its primary sources. One of the keys to the success of the framework in Figure 1-1 is the identification of secondary components, for which further understanding is required. This will be accomplished in Task 2.7 via an analysis of location-specific ambient data from both the season-specific field programs and the annual field program. For

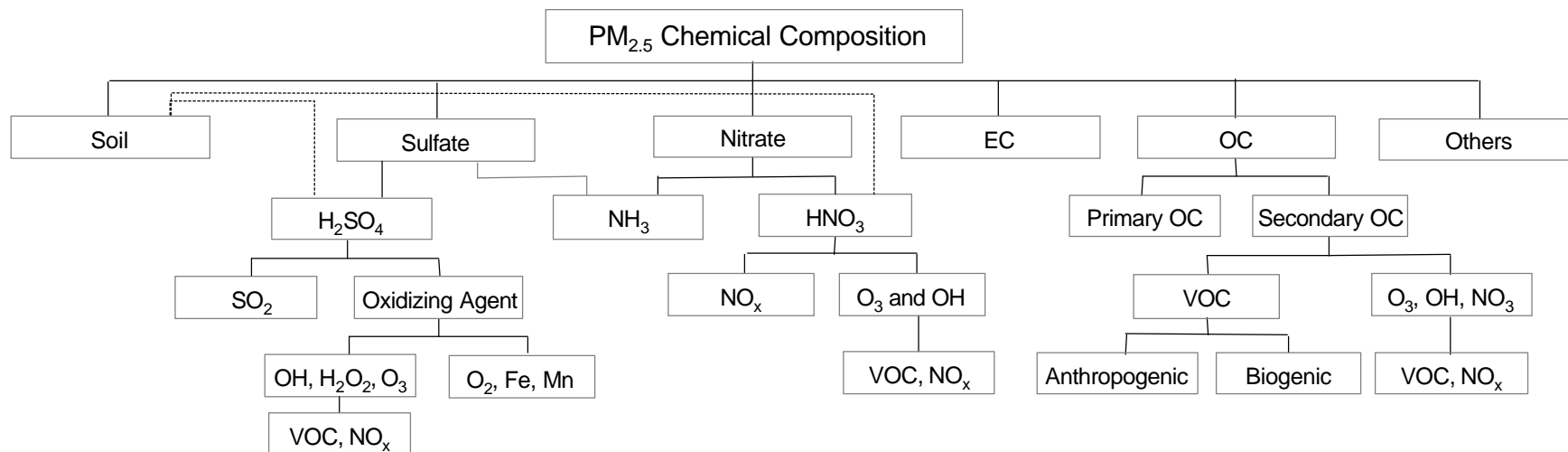


Figure 1-1. Analysis of chemical transformations (adapted from Pun and Seigneur, 1999).

secondary compounds, we intend to trace their formation and identify the rate-limiting reagents. In Task 6.1, we will study the phase partition of PM and their precursors using several thermodynamic models. This will allow us to identify if the chemistry or the partition is limiting the formation of some volatile components of PM, such as nitrate. We have determined for IMS 95 that ammonia was relatively abundant. Therefore, the formation of PM nitrate was limited by nitric acid. In Task 6.2, we will use models, such as SCAPE2 and an advanced cloud chemistry model to confirm that finding.

Although we have postulated that the formation of nitric acid was sensitive to concentrations of oxidants in the urban areas of the SJV based on modeling results (Pun and Seigneur, 2001a), the atmospheric chemistry in rural areas may be  $\text{NO}_x$  limited (Stockwell et al., 2000). A complete understanding requires the knowledge of the locations where nitrate formation takes place as well as the mechanism through which it is dispersed throughout the SJV. Watson and Chow (2001) postulated the role of aloft transport in the dispersion of PM nitrate. Task 6.3 will provide some insights on those issues.

We will use data and modeling to confirm the parts of the previous conceptual model on sulfate and SOA. The former may be oxidant limited. For the latter, we will draw on the analyses done in Task 2 and 4 of the current RfP. Other major knowledge gaps in dispersion and dry deposition will be filled, to the extent possible, using the analyses in Task 6.

In addition, it is important to elucidate to the extent possible the relationship between secondary PM components (e.g., sulfate, nitrate) and  $\text{O}_3$ . A solid understanding will ensure that the strategies to reduce oxidants and PM can be coordinated to provide the maximum air quality benefit.

## 2. TECHNICAL APPROACH

### 2.1 Task 2.7

#### 2.1.1 Where and when do elevated ozone concentrations correspond to excessive PM<sub>2.5</sub> concentrations?

The relationships between ozone and PM are of interest because ozone and components of PM are governed by the same gaseous precursors. Therefore, control measures placed on PM necessarily have implications towards ozone concentrations. In the SJV, high ozone concentrations are typically observed in the summer, while high PM concentrations are typically experienced in the fall (PM<sub>10</sub>) and winter (PM<sub>2.5</sub>). Considering the absolute levels, elevated ozone and elevated PM probably only occur together during spring and fall. However, within a given season, there may be correlations between ozone and PM. CRPAQS provides a unique opportunity to study the relationship between PM<sub>2.5</sub> and other photochemical oxidants because of the comprehensive nature of the measurements at the core sites and the availability of data from different seasons.

We propose to analyze the PM and ozone data for different seasons at three core sites, Angiola Tower, Fresno, and Bakersfield. A fourth site is equipped with both ozone and PM measurements during the winter study in the Sierra Nevada foothills. Within each season, the relationships between ozone and PM will be elucidated using correlation analyses of the deviations from the mean values. While the relationship between ozone and PM may be obscured by seasonality, we hypothesize some possible season-specific relationship as follows. In summer, the temperature is high, which is not favorable for the formation of ammonium nitrate. However, one might expect elevated PM concentrations during ozone episodes because of the effects of elevated oxidant concentrations on the formation of SOA. A correlation analysis of ozone with PM OC will be performed to test this hypothesis. The results may be different in urban locations that have abundant NO<sub>x</sub> emissions and rural locations that may be more abundant in biogenic VOC concentrations.

During winter, PM nitrate is a dominant component of PM<sub>2.5</sub>. Pun and Seigneur (2001a) postulated the importance of the nighttime ozone reaction in the formation of PM nitrate under some episodic conditions. One way to test this hypothesis may be to correlate PM and PM nitrate concentrations to ozone, especially the ozone concentrations in the evening. The results at urban and rural locations are expected to differ due to different degrees of NO<sub>x</sub> vs. oxidant sensitivities.

During several fog episodes of IMS 95, ozone played an important role in the aqueous oxidation of SO<sub>2</sub> to sulfate (Lillis et al., 1999). Therefore, the formation of sulfate may correlate with the concentrations of ozone during a fog episode, especially in locations where the aqueous-phase oxidation of SO<sub>2</sub> is limited by oxidants. Such an analysis can be used to confirm the findings of Lillis et al. that sulfate production tended to be limited by the availability of oxidants in urban areas.

The statistical significance of the regression analyses will be tested using standard or advanced statistical procedures such as bootstrap resampling.

### 2.1.2 What fraction of the PM<sub>2.5</sub> corresponds to photochemical end-products?

Photochemical end products in PM<sub>2.5</sub> include sulfate, nitrate, ammonium, and SOA. The inorganic components are measured at all core sites, and those measurements will be analyzed to determine the seasonality and temporal and geographical variabilities of secondary inorganic PM components.

A key knowledge gap is in SOA formation. At present, there is no experimental technique that can segregate primary compounds from secondary compounds. We propose to use two different approaches to estimate the concentration of SOA. The first one is the so-called black carbon/organic carbon (BC/OC) approach. Since BC is expected to be predominantly primary in nature, it is often used as a tracer of primary organic aerosols (POA). The assumption made with this technique is that BC and POA have the same sources, and a representative ratio of POA to BC exists for a given region. This representative ratio can be determined from the emission inventory for primary compounds. However, we do not expect the final PM inventory for CRPAQS to be available during the initial data analysis phase. In order to determine this ratio, we will take advantage of the hourly OC and BC measurements at the core sites. The ambient ratio of OC to BC will be plotted as a function of time. When photochemical activity is low, we can determine a minimum OC/BC ratio at that site that corresponds to the mixture or primary emissions. If the ambient value of the OC to BC ratio is greater than the characteristic value of the POA to EC ratio, the excess OC consists of SOA (Turpin and Huntzicker, 1995). The main drawback of this technique is that previously formed SOA may be present in the region during a stagnation episode and the SOA background may significantly skew measured POA to BC ratios.

As a second approach, the “unapportioned” OC in source apportionment studies (from Task 4) may be used to provide an estimate of SOA. We can corroborate the findings of the OC/BC approach once the source apportionment analysis is complete. If the results prove inconsistent, one way to refine the SOA estimate based on the OC/BC approach would be to calculate a representative primary emission ratio based on the sources, their profiles and the contributions identified for that site, either from the receptor modeling, or if available at this later stage of the project, PM emission inventories. The results from two methods will be compared and our estimates of SOA will be presented with the corresponding uncertainties.

## 2.2 Task 6.1

The objective of this task is to characterize and explain the distribution of chemical species among the gas, particulate and liquid phases in the San Joaquin Valley (SJV) during CRPAQS. Variability of this phase distribution as a function of space within the valley and time during CRPAQS must be addressed. The effect of fog events is also of great interest because of their frequent occurrence during winter in the SJV.

Our technical approach will consist of several subtasks. First, we will assemble the relevant data from the aerometric database. Next, we will analyze these data for gas/particle partitioning of chemical species in the absence of fog as a function of meteorological conditions (temperature and relative humidity), location and time. We will then simulate the gas/particle partitioning with comprehensive thermodynamic